J Therm Anal Calorim (2016) 123:1091–1098
DOI 10.1007/s10973-015-5044-8

Comparative study of zinc addition effect on thermal properties of silicate and phosphate glasses

J. Sułowska[1] · I. Wacławska[1] · M. Szumera[1]

Received: 30 April 2015 / Accepted: 14 September 2015 / Published online: 3 October 2015

Abstract The aim of the study was an analysis of two groups of glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO system with various content of network formers in the form of P_2O_5 and SiO_2, modified by the addition of ZnO. Their effect on glass-forming ability, glass transition effect, crystallization process and the kind of crystallizing phases was examined using DSC and XRD methods. It was observed that in both matrixes, the addition of ZnO decreases the glass transition temperature (T_g). The lower T_g values observed in the phosphate matrix glasses and the accompanying higher values of the changes in molar heat capacity (Δc_p) in contrast to the silicate matrix glasses may be considered an indicator of the degree of the reconstruction of their amorphous structure, which facilitates the process of their crystallization. It was found that the crystallizing products of the silicate matrix glasses were silicates and phosphates whose structure contained zinc. In the phosphate matrix glasses, it was observed that zinc inhibited the crystallization of silicate phases.

Keywords Silicate–phosphate glasses · ZnO · Glass transition · Thermal stability · Crystallization

Introduction

Phosphate and silicate glasses containing zinc have been studied intensively, because many of them have been found useful for special applications.

✉ J. Sułowska
sulowska@agh.edu.pl

[1] Department of Ceramics and Refractories, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, A. Mickiewicza 30, 30-059 Kraków, Poland

Zinc phosphate glasses have been developed for use as LED light sources [1, 2] and as substrates for optical waveguides written by f-sec lasers [3–6]. Zinc phosphate glasses also tend to have greater coefficients of thermal expansion with low processing temperatures, which makes them useful as sealing glasses [7, 8]. Because zinc is a trace element that plays an important role in bone formation and mineralization [9, 10], zinc-containing glasses and glass ceramics have been developed for bone engineering applications [11–13]. Zinc has also been cited as a useful antibacterial agent in glass-ionomer-based cements [14] and ceramic coatings [15]. Thus, the addition of zinc to various materials and their use in bone tissue engineering may have important implications for appropriate integration into implant sites with minimal bone infection risk, a complication often associated with the repair of skeletal defects.

It is a well-known fact that the ability to absorb components that function as modifiers is much higher in the phosphate matrix glasses than in the silicate matrix glasses. The ability to take the amorphous form also depends on the kind of introduced modifiers [16, 17]. The works [18–20] show that it is possible to add up to 80 mol% of ZnO into the structure of the glasses from the system P_2O_5–ZnO. Examining the scope of forming silicate glasses modified with ZnO, Kaur et al. [21] produced silicate glass with the composition $40SiO_2$–$30BaO$–$20ZnO$–$10B_2O_3(Al_2O_3)$, and Hurt and Philips [22] introduced 35 mol% ZnO into the structure of the glasses from the Na_2O–ZnO–SiO_2 system. The research done by Minser et al. [23] shows that it is possible to obtain fully amorphous glass from the Na_2O–ZnO–SiO_2 system if it contains the addition of ZnO in the amount of up to 30 % mol. The research on the glasses with the composition $(100-x)SiO_2$–$7CaO$–$5K_2O$–$19Na_2O$–xZnO done by Chen et al. [24] indicates that adding over 19 mol% of ZnO causes their crystallization.

There is little information in the literature about the possibility of introducing zinc into the structure of silicate–phosphate glasses. Goel et al. [25] introduced the additive ZnO into the structure of glasses composed of 36.07CaO–(19.24−*x*)MgO–*x*ZnO–5.61P_2O_5–38.49SiO_2–0.59CaF_2, where $x \leq 10$ mol%, produced in the traditional melting process, and Aina et al. [26], employing the same method for the synthesis, obtained fully amorphous glass containing 20.2 mass% ZnO and 37.3 % SiO_2, 18.8 % Na_2O, 18.9 % CaO, 4.5 % P_2O_5 (mass%). In the literature, there are also references on the ability to form silicate–phosphate glasses that contain ZnO and are precursors of glass–crystalline materials to which P_2O_5 was added as a nucleating agent. An example is the work of Demirkesen et al. [27] who obtained fully amorphous silicate glass with the composition 10Li_2O–32ZnO–55SiO_2–3P_2O_5 (mass%).

There is little information in the literature on the influence of the addition of ZnO on thermal properties of silicate and phosphate glasses, and even less on silicate–phosphate glasses.

The authors [28] examined the transformation of the vitreous state of the glasses with the composition 50P_2O_5–(40−*x*CaO)–10Na_2O–*x*ZnO, where $x \leq 20$ mol%. Their research shows that adding increased amounts of ZnO caused a linear decrease in the values of the transition temperature (T_g) of those glasses. According to the authors, it resulted from the formation of weaker Zn–O–P bonds that replace Ca–O–P bonds and from the decrease in the crosslink density of those glasses. Thermal test carried out on the glasses with the composition $(MnO)_x{\cdot}(P_2O_5)_{40}{\cdot}(ZnO)_{60-x}$ where $x = 0$–20 % mol. [29] showed that a gradual decrease in ZnO content in the structure of the above-mentioned glasses caused a slight decrease in the T_g, yet all T_g values were close to 415 °C so zinc phosphate matrix is poorly affected by the substitution of ZnO with MnO up to 20 mol%. On the other hand, thermal tests of glasses with the compositions (50−*x*)ZnO·*x*MgO·50P_2O_5 ($0 \geq x \geq 50$) and (60−*y*)ZnO·yMgO·40P_2O_5 ($0 \geq x \geq 60$) [30] indicate that a gradual decrease in the content of ZnO and the simultaneous increase in the content of MgO cause an increase in the T_g value from ∼450 to ∼600 °C. Testing glasses from the system Li_2O–ZnO–Al_2O_3–SiO_2, Demirkesen and Maytalman [31] observed an increase in the T_g value of the glasses parallel to the decrease in the content of ZnO with the simultaneous increase in the amount of the introduced Al_2O_3. This behaviour can be attributed to strengthening of the bonds within the glass network upon replacement of ZnO by Al_2O_3. The research done by the authors [32] indicates that the increased addition of ZnO into the structure of bioactive silicate–phosphate glass from the SiO_2–CaO–Na_2O–P_2O_5–ZnO system at the expense of the simultaneous decrease in the content of CaO and Na_2O does not cause major changes in the T_g value or in the crystallization temperature of those glasses.

The object of those studies was silicate–phosphate glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO system which can act as slow-dissolving fertilizers providing plant macroelements (P, K, Ca, and Mg) [33], as well as zinc acting as microelement. Zinc plays an active role in many life processes of plants, including the metabolism of carbohydrates, proteins, and phosphorus compounds. It also influences the synthesis of auxins, regulates the formation of ribosomes, and affects the permeability of cell membranes [34].

The presented work includes the results of comparative studies on the influence of the addition of zinc ions introduced at the expense of the decrease in the amount of calcium and magnesium on the glass-forming ability and the thermal characteristics of the glasses from the above-mentioned system, with different content of such network formers as SiO_2 and P_2O_5.

Experimental

Two groups of glasses from SiO_2–P_2O_5–K_2O–CaO–MgO system differing in glass network formers content (the Si group of glasses and the P group of glasses) modified by ZnO addition were prepared. In each group of glasses, constant quantities of SiO_2, P_2O_5, and K_2O were kept and increasing amount of ZnO was introduced at the cost of decreasing amount of MgO and CaO, with the constant MgO/CaO ratio. The glasses were produced by melting the mixture of raw materials, i.e. SiO_2, $(NH_4)_2HPO_4$, K_2CO_3, MgO, $CaCO_3$, and ZnO in platinum crucibles at 1100 °C (the phosphate glasses) and at 1450 °C (the silicate glasses). The obtained glasses were ground to 0.1- to 0.3-mm grain size.

The chemical composition of the synthesized glasses was determined by the X-ray fluorescence spectrometry (XRF) method, using the ARL Advant'XP spectrometer.

The X-ray diffraction method was used to confirm the amorphous state of the samples using X'Pert Pro Diffractometer (Phillips) with a step of 0.008° and collecting time 45 s.

Thermal stability of the obtained glasses was determined by DSC measurements conducted on STA 449 F3 Jupiter 7 (Netzsch) operating in the heat flux DSC mode. The temperature and heat calibrations of the instrument were performed using the melting temperatures and melting enthalpies of high-purity aluminium, tin, zinc, silver, and gold. The samples (∼40 mg) were heated in platinum crucibles at 10 °C min^{-1} in dry nitrogen atmosphere up to 1100 °C. The glass transformation temperature T_g determined as the midpoint of the c_p changes in the glass

transformation region and changes in specific heat (Δc_p) accompanying the glass transformation was determined by applying the Netzsch Proteus Thermal Analysis Program (version 5.0.0.). The ability of glasses to crystallize was evaluated from the values of the thermal stability parameter of glasses (ΔT) determined as:

$$\Delta T = T_{onset} - T_g$$

where T_{onset} is the onset temperature of the first crystallization stage and T_g is the glass transition temperature of the given sample.

The samples containing the particle size of 0.1–0.3 mm were isothermally heated for 5 h at the crystallization temperatures that were inferred from DSC measurements. The temperature stability was better than ±5 °C. The resulted crystalline phases were detected and identified by XRD method.

Results and discussion

Homogeneous, transparent glasses were obtained from all compositions studied. The nominal chemical composition of the glasses determined by the X-ray fluorescence spectrometry (XRF) method is presented in Table 1.

The chemical analysis of the chosen glasses showed a satisfying conformance of their assumed and real chemical compositions. Therefore, it was assumed that the chemical compositions of all melted glasses fulfil the assumptions.

Glass-forming ability

The XRD tests (Fig. 1) showed that all obtained glasses are fully amorphous in the concentration range in question. Hence, the solubility of ZnO in the structure of the glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO system in the examined concentration range does not depend on the content of network formers (SiO_2, P_2O_5).

Glass transition

During heating and cooling, vitreous substances exhibit glass transition effect which is induced by relaxation of stresses being the consequence of a disordered arrangement of the atoms forming the glass structure. The relaxation of stresses in the glass structure taking place at transition temperature (T_g) is related to a change in such properties as heat capacity, linear and volume expansion coefficients, and viscosity. Parameters characterizing the glass transition effect depend on the nature and the number of components forming the glassy structure.

The DSC tests showed that the increase in the addition of ZnO into the structure of both glass groups causes a gradual decrease in their T_g value (Fig. 2a, b). The T_g values are higher by about 150 °C in the silicate matrix glasses (41Si) (Fig. 3) than in the phosphate matrix glasses (41P).

Regardless of the vitreous matrix, the decrease in the T_g value was accompanied by a decrease in the Δc_p value, which was better visible in the glasses with the higher content of SiO_2 (Table 2).

The changes in the glass transition temperature values (T_g) could be explained based on the nature of chemical bonds in the structure of the glasses. The ionicity (i_G) value of the bonds of the component atoms with oxygen according to Görlich's scale [35] was applied as a parameter characterizing the strength of the bonds. It increases with decreasing iconicity. Another parameter is the localization of the bonding electron "L" $= \overline{Z_{eff}} = \sqrt{Z_{eff1} \cdot Z_{eff2}}$ [35]. Its value increases with the covalence of the bonds

Table 1 Nominal chemical composition of glasses and determined by the X-ray fluorescence spectrometry (XRF) (in brackets) in mol%

Group of glasses	Glass name	SiO_2	P_2O_5	K_2O	CaO	MgO	ZnO
The Si group	0Zn41Si	41	6	6	19	28	
	2Zn41Si	41 (37.6)	6 (5.7)	6 (7.5)	18 (19.1)	27 (27.8)	2 (2.3)
	4Zn41Si	41 (37.9)	6 (5.6)	6 (7.5)	17 (18.0)	26 (26.7)	4 (4.3)
	8Zn41Si	41 (38.0)	6 (6.1)	6 (7.3)	16 (17.2)	23 (23.1)	8 (8.3)
	15Zn41Si	41	6	6	13	19	15
	30Zn41Si	41	6	6	7	10	30
The P group	0Zn41P	6 (6.3)	41 (41.2)	6 (6.2)	19 (19.6)	28 (26.7)	
	2Zn41P	6	41	6	18	27	2
	4Zn41P	6 (5.8)	41 (41.5)	6 (6.1)	17 (17.4)	26 (25.1)	4 (4.1)
	8Zn41P	6	41	6	16	23	8
	15Zn41P	6 (5.3)	41 (40.6)	6 (5.8)	13 (13.8)	19 (18.2)	15 (16.3)
	30Zn41P	6	41	6	7	10	30

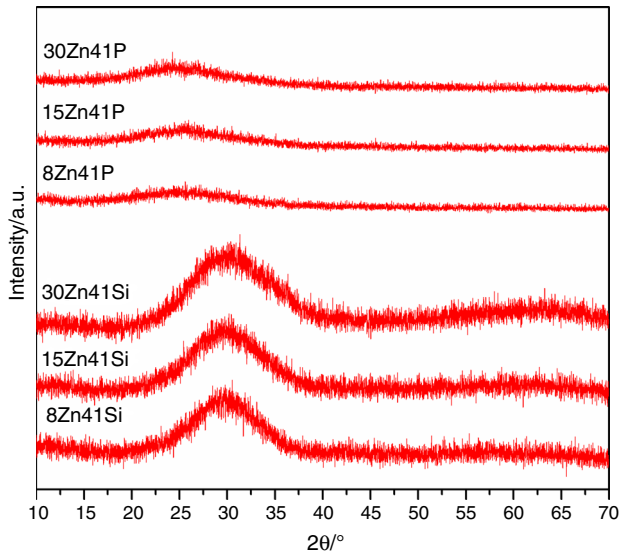

Fig. 1 XRD patterns of the glasses

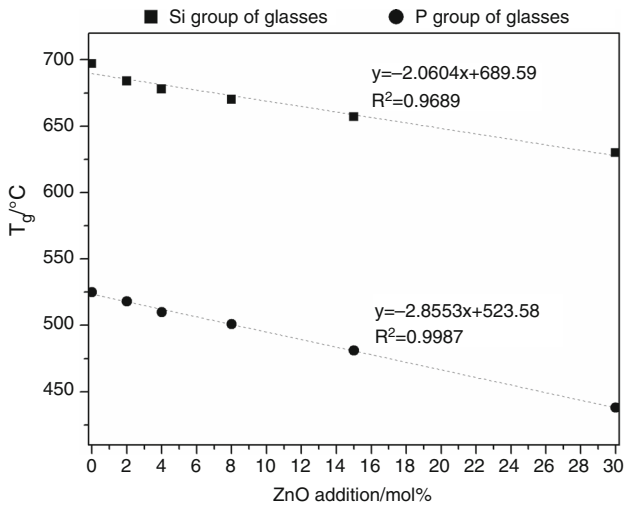

Fig. 3 Glass transition temperature values (T_g) versus molar concentration of ZnO in the structure of the studied glasses

with oxygen, and this parameter has been accepted as a measure of the rigidity of the bonds. The more covalent character of Zn–O bonds ($i_G = 0.639$, $L = 1.914$) replacing the more ionic bonds such as Ca–O bonds ($i_G = 0.707$, $L = 1.725$) and Mg–O bonds ($i_G = 0.670$, $L = 1.830$) made the glass structure more rigid the consequence of which was increased stress in the glass. Its relaxation required less energy and hence lower T_g value with the increase in the content of ZnO in the structure of both types of glasses. Simultaneously, due to the more covalent character of P–O bonds ($i_G = 0.314$, $L = 2.640$) compared to Si–O bonds ($i_G = 0.428$, $L = 2.410$), the phosphate matrix glasses show lower T_g temperature values than silicate matrix glasses. The relaxation of more stresses in the structure of phosphate matrix glasses (41P) than in the structure of silicate matrix glasses (41Si) was accompanied by a slightly higher change in the Δc_p parameter accompanying the transition of the vitreous state.

Crystallization

The thermal tests carried out on the analysed glasses allowed to determine the influence of the increasing addition of ZnO and the network formers on their

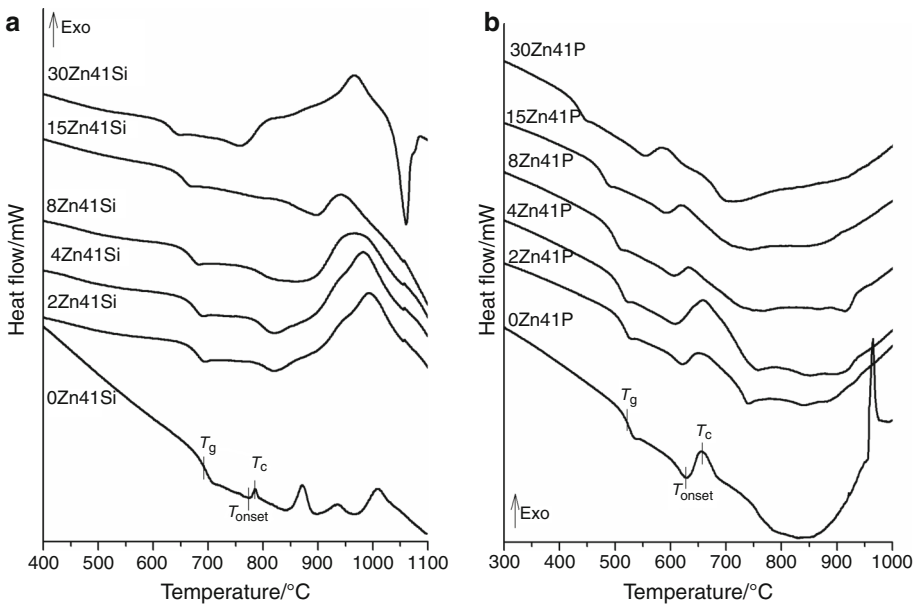

Fig. 2 DSC curves of the **a** Si group and **b** P group of glasses

Table 2 Thermal characteristic of the transition of vitreous state and the thermal durability of the glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO system modified with the addition of ZnO at the expense of the simultaneous decrease in the content of CaO and MgO

Glass name	T_g/°C	Δc_p/J g^{-1} K^{-1}	ΔT/°C	Glass name	T_g/°C	Δc_p/J g^{-1} K^{-1}	ΔT/°C
0Zn41Si	697	0.31	81	0Zn41P	525	0.27	112
2Zn41Si	684	0.24	138	2Zn41P	518	0.29	109
4Zn41Si	678	0.26	144	4Zn41P	510	0.29	109
8Zn41Si	670	0.25	193	8Zn41P	501	0.33	109
15Zn41Si	657	0.19	242	15Zn41P	481	0.26	119
30Zn41Si	630	0.17	131	30Zn41P	438	0.23	120

crystallization ability determined based on the ΔT parameter (Table 2).

It was observed that the crystallization ability of the phosphate matrix glasses (41P) modified by ZnO addition is higher than crystallization ability of the silicate matrix glasses (41Si). The crystallization ability of 41Si glasses decreases with increasing amount of ZnO up to 15 mol% addition, while the addition of 30 mol% of ZnO causes the rapid reduction in ΔT parameter value.

In reference to the already conducted analysis of the atomic reactions in the structures of the examined glasses, based on the characteristic of the nature of the formed chemical bonds, it should be noted that lower T_g values accompanied by higher Δc_p values that are related to the reduction in structural stresses (breaking chemical bonds) are equivalent to the higher level of reconstruction of the amorphous structure of the glass which takes place before the crystallization process. Hence, the phosphate matrix glasses have lower thermal stability and higher crystallization ability compared to the silicate matrix glasses. The glass transition effect expressed with such parameters as T_g and Δc_p may be treated as an indicator of the level of the reconstruction of the disordered structure of glasses towards their crystallization [36].

The DSC curves of glasses (Fig. 2a, b) show that the crystallization of the base glasses (0Zn) from the two examined groups of glass was a multi-stage process with four stages (Si group glass) and two stages (P group glass). The introduction of the increasing amount of ZnO to the composition of the studied glasses changed the character of exothermal effects whose number was reduced and they were overlapping.

The analysis of the crystallization products of the silicate matrix glasses showed that the main crystallizing phases found in the base glass (0Zn41Si) are orthophosphate of $Ca_9MgK(PO_4)_7$ type and disilicate of $CaMgSi_2O_6$ type (Table 3).

It was found that the increasing amount of zinc ions in the structure of those glasses facilitates the formation of $Ca_9ZnK(PO_4)_7$ orthophosphate during their crystallization (Fig. 4). It was also observed that the increase in the content of ZnO in the structure of the studied glasses caused a diversification of crystallization products in the form of silicates. Apart from $CaMgSi_2O_6$-type silicate (diopside), the crystallization products included Mg_2SiO_4-type orthosilicate (forsterite) and an orthosilicate containing zinc Zn_2SiO_4 (willemite).

The XRD study of the base glass with phosphate matrix (0Zn41P) (Table 3) showed that the crystallization products of the glass are polyphosphate compounds composed of $KMg(PO_3)_3$ and $CaMgP_2O_7$. The type of the formed phosphate networks conforms to the structural classification of phosphate glasses based on the *O*/*P* ratio [37]. In the group of the tested phosphate matrix glasses, the *O*/*P* ratio was 3.3, which conforms to the structures typical of meta- and pyrophosphates.

The increase in the amount of ZnO up to 15 mol% apart from the above-mentioned types of phosphates results in the formation of pyrophosphates containing zinc, such as $K_2ZnP_2O_7$ (Fig. 5). For the glass 30Zn41P, there is no evidence of crystallization of $KMg(PO_3)_3$ and $CaMgP_2O_7$ compounds, but apart from the formation of $K_2ZnP_2O_7$, the appearance of magnesium-rich metaphosphate of $Mg_2P_4O_{12}$ type was detected.

It should also be noted that the introduction of increasing amounts of ZnO into the structure of phosphate matrix glasses inhibits the crystallization of silicate phases.

It was found that the succession of the appearance of the crystallization products in the form of phosphates and silicates in the analysed glasses (Table 4) resulted from the value of Gibbs free enthalpy in the formation of phosphates and silicates from oxides (ΔG) which determines the probability of their formation (Table 4).

Table 3 X-ray characteristics of crystallization process of analysed glasses

Glass name	T_c/°C	Crystalline phase (ICSD code)
0Zn41Si	786	$Ca_9MgK(PO_4)_7$ (88-0798)
	872	$Ca_9MgK(PO_4)_7$ (88-0798)
	935	$Ca_9MgK(PO_4)_7$ (88-0798)
		$CaMgSi_2O_6$ (03-0522)
	1010	$CaMgSi_2O_6$ (03-0522)
		$Ca_9MgK(PO_4)_7$ (88-0798)
2Zn41Si	1000	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Mg_2SiO_4 (85-1346)
		$CaMgSi_2O_6$ (03-0522)
4Zn41Si	1000	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Mg_2SiO_4 (85-1346)
		$CaMgSi_2O_6$ (03-0522)
8Zn41Si	980	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Mg_2SiO_4 (85-1346)
		$CaMgSi_2O_6$ (03-0522)
15Zn41Si	960	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Mg_2SiO_4 (85-1346)
		Zn_2SiO_4 (37-1485)
30Zn41Si	820	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Zn_2SiO_4 (37-1485)
	980	$Ca_9MgK(PO_4)_7$ (88-0798)
		$Ca_9ZnK(PO_4)_7$ (50-0344)
		Zn_2SiO_4 (37-1485)
0Zn41P	660	$KMg(PO_3)_3$ (18-1038)
		$CaMgP_2O_7$ (24-0135)
	970	$CaMgSi_2O_6$ (03-0522)
2Zn41P	664	$KMg(PO_3)_3$ (18-1038)
		$CaMgP_2O_7$ (24-0135)
		$K_2ZnP_2O_7$ (34-0442)
4Zn41P	662	$KMg(PO_3)_3$ (18-1038)
		$CaMgP_2O_7$ (24-0135)
		$K_2ZnP_2O_7$ (34-0442)
8Zn41P	635	$KMg(PO_3)_3$ (18-1038)
		$CaMgP_2O_7$ (24-0135)
		$K_2ZnP_2O_7$ (34-0442)
15Zn41P	625	$KMg(PO_3)_3$ (18-1038)
		$CaMgP_2O_7$ (24-0135)
		$K_2ZnP_2O_7$ (34-0442)
30Zn41P	593	$K_2ZnP_2O_7$ (34-0442)
		$Mg_2P_4O_{12}$ (40-0067)
		$CaMgP_2O_7$ (24-0135)

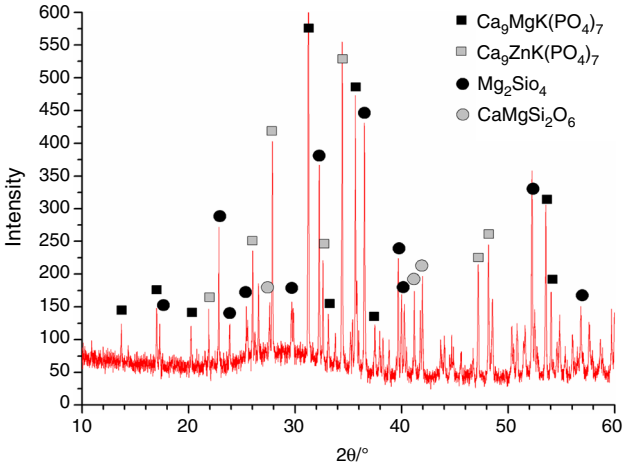

Fig. 4 XRD pattern of the 8Zn41Si glass after heating at 980 °C

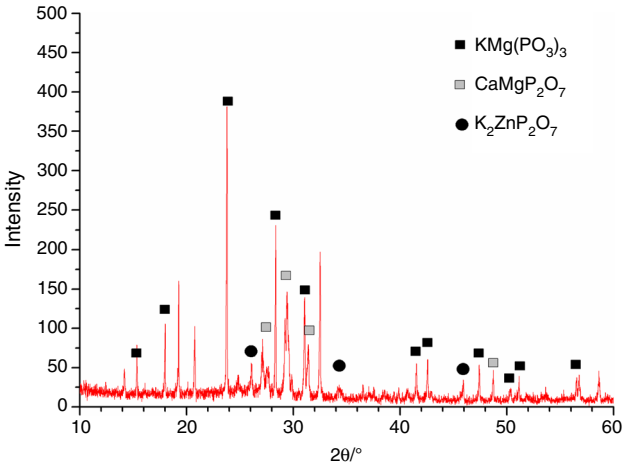

Fig. 5 XRD pattern of the 8Zn41P glass after heating at 635 °C

Table 4 Values of ΔG_f° of the formation of phosphates and silicates crystallizing in analysed glasses [38]

Compounds	ΔG_f°/kJ mol^{-1}		
	900 K	1000 K	1100 K
$Ca_9MgK(PO_4)_7$	−18,846	−19,196	−19,563
$Ca_9ZnK(PO_4)_7$	−18,622	−18,842	−19,343
$Mg_2P_4O_{12}$	−8012	−8093	−8332
$KMg(PO_3)_3$	−5930	−5997	−6182
$CaMgP_2O_7$	−4695	−4746	−4875
$K_2ZnP_2O_7$	−4253	−4316	−4459
$CaMgSi_2O_6$	−3271	−3311	−3354
Mg_2SiO_4	−2255	−2282	−2311
Zn_2SiO_4	−1782	−1815	−1846

Conclusions

Thermal properties of SiO_2–P_2O_5–K_2O–CaO–ZnO glasses with various contents of SiO_2, and P_2O_5 were investigated. The increased amount of ZnO-replaced MgO and CaO in the structure of glasses with both silicate and phosphate matrixes caused decrease in T_g temperature. The lower T_g values observed in the phosphate matrix glasses and the accompanying higher changes in molar heat capacity (Δc_p) in contrast to silicate matrix glasses may be regarded as an indicator of the level of transition of their amorphous structure, which facilitates their crystallization. It was found that the increasing amount of zinc in the structure of both groups of glasses facilitates the formation of complex phosphates containing zinc, which took place during their crystallization. On the other hand, the increasing amount of zinc in the structure of the silicate matrix glasses caused the diversification of crystallization products in the form of silicates containing zinc in contrast to the phosphate matrix glass in which the inhibiting effect of zinc on the crystallization of the silicate phases was observed. The nature of the studied thermal transitions is in accordance with the kinds of bonds in the analysed glasses (crystallochemical factors) and Gibbs free enthalpy of the formation of crystalline compounds (chemical affinity of the glass components).

Acknowledgments The work was supported by Faculty of Materials Science and Ceramics AGH—University of Science and Technology No 11.11.160.617.

References

1. Martinez-Martinez R, Speghini A, Bettinelli M, Falcony C, Caldino U. White light generation through the zinc metaphosphate glass activated by Ce^{3+}, Tb^{3+} and Mn^{2+} ions. J Lumin. 2009;129:1276–80.
2. Eriah E, Bhat SG. Optical properties of samarium doped zinc-phosphate glasses. J Phys Chem Solids. 2007;68:581–5.
3. Fletcher LB, Witcher JJ, Troy N, Reis ST, Brow RK, Krol DM. Effects of rare-earth doping on femtosecond laser waveguide writing in zinc polyphosphate glass. J Appl Phys 2012;112:023109.1-6.
4. Fletcher LB, Witcher JJ, Troy N, Reis ST, Brow RK, Vazques RM, Osellame R, Krol DM. Femtosecond laser writing of waveguides in zinc phosphate glasses. Opt Mater Express. 2011;1:845–55.
5. Fletcher LB, Witcher JJ, Troy N, Reis ST, Brow RK, Krol DM. Direct femtosecond laser waveguide writing inside zinc phosphate glass. Opt Mater Express. 2011;19:7929–36.
6. Canioni L, Bellec M, Royon A, Bousquet B, Cardinal T. Three-dimensional optical data storage using third-harmonic generation in silver zinc phosphate glass. Opt Lett. 2008;33:360–2.
7. Wilder JA Jr. Glasses and glass ceramics for sealing to aluminum alloys. J Non-Cryst Solids. 1980;388 & 339:879–84.
8. Morena RM. Phosphate glasses as alternatives to Pb-based sealing frits. J Non-Cryst Solids. 2000;263 & 264:382–7.
9. Hall SL, Dimai HP, Farley JR. Effects of zinc on human skeletal alkaline phosphatase activity in vitro. Calcif Tissue Int. 1999;64:163–72.
10. Wu X, Itoh N, Taniguchi T, Nakanishi T, Tatsu Y, Yumoto N, Tanaka K. Zinc-induced sodium-dependent vitamin C transporter 2 expression: potent roles in osteoblast differentiation. Arch Biochem Biophys. 2003;420:114–20.
11. Ramswamy Y, Wu C, Zhou H, Zreiquat H. Biological response of human bone cells to zinc-modified Ca-Si based ceramics. Acta Biomater. 2008;3:1487–97.
12. Ito A, Ojima K, Natio H, Ichinose N, Tateischi T. Preparation, solubility and cytompatibility of zinc-releasing calcium phosphate ceramics. J Biomed Mater Res. 2000;50:178–83.
13. Salih V, Patel A, Knowles JC. Zinc-containing phosphate-based glasses for tissue engineering. Biomed Mater. 2007;2:11–20.
14. Osinaga PW, Grande RH, Ballester RY, Simionato MR, Delgado Rodrigues CR, Muench A. Zinc sulfate addition to glass-ionomer-based cements: influence on physical and antibacterial properties, zinc and fluoride release. Dent Mater. 2003;19:212–7.
15. Bright KR, Gerba CP, Rusin PA. Rapid reduction of Staphylococcus aureus populations on stainless steel surfaces by zeolite ceramic coatings containing silver and zinc ions. J Hosp Infect. 2002;52:307–9.
16. Szumera M, Wacławska I. Effect of molybdenum addition on the thermal properties of silicate–phosphate glasses. J Therm Anal Cal. 2012;109:649–55.
17. Sułowska J, Wacławska I, Szumera M. Effect of copper addition on glass transition of silicate–phosphate glasses. J Therm Anal Cal. 2012;109:705–10.
18. Takebe H, Baba Y, Kuwabara M. Dissolution behavior of ZnO–P_2O_5 glasses in water. J Non-Cryst Solids. 2006;352:3088–94.
19. Wiench J, Pruski M, Tischendorf B, Otaigbe J, Sales B. Structural studies of zinc polyphosphate glasses by nuclear magnetic resonance. J Non-Cryst Solids. 2000;263–264:101–10.
20. Tischendorf B, Otaigbe J, Wiench J, Pruski M, Sales B. A study of short and intermediate range order in zinc phosphate glasses. J Non-Cryst Solids. 2001;282:147–58.
21. Kaur G, Sharma P, Kumar V, Singh K. Assessment of in vitro bioactivity of SiO_2–BaO–ZnO–B_2O_3–Al_2O_3 glasses: an optico-analytical approach. Mater Sci Eng, C. 2012;32:1941–7.
22. Hurt J, Philips C. Structural role of zinc oxide in glasses in the system Na_2O–ZnO–SiO_2. J Am Ceram Sci. 1970;53:269–73.
23. Minser D, Walden B, White W. Structure of alkali-zinc silicate glasses by Raman Spectroscopy. Commun Am Ceram Sci. 1984:C-47.
24. Chen X, Brauer D, Karpukhina N, Waite R, Barry M, McKay I, Hill R. 'Smart' acid-degradable zinc-releasing silicate glasses. Mater Lett. 2014;126:278–80.
25. Goel A, Kappor S, Tilocca A, Rajagopal R, Ferreira M. Structural role of zinc in biodegradation of alkali-free bioactive glasses. J Mater Chem B. 2013;1:3073–82.
26. Aina V, Malavasi G, Fiorio Pla A, Munaron L, Morterra C. Zinc-containing bioactive glasses: surface reactivity and behaviour towards endothelial cells. Acta Biomater. 2009;5:1211–22.

27. Demirkesen E, Maytalman E. Effect of Al_2O_3 additions on the crystallization behaviour and bending strength of Li_2O–ZnO–SiO_2 glasses. J Non-Cryst Solids. 2001;27:287–93.
28. Abou Neel EA, O'Dell LA, Smith ME, Knowles JC. Processing, characterisation, and biocompatibility of zinc modified metaphosphate based glasses for biomedical applications. J Mater Sci Mater Med. 2008;19:1669–79.
29. Pascuta P, Bosca M, Borodi G, Culea E. Thermal, structural and magnetic properties of some zinc phosphate glasses doped with manganese ions. J Alloy Compd. 2011;509:4314–9.
30. Smith CE, Brow RK. The properties and structure of zinc magnesium phosphate glasses. J Non-Cryst Solids. 2014;390:51–8.
31. Demirkesen E, Maytalman E. Effect of Al_2O_3 additions on the crystallization behavior and bending strength of a Li_2O–ZnO–SiO_2 glass-ceramic. Ceram Int. 2001;27:99–104.
32. Wers E, Oudadesse H. Thermal behavior and excess entropy of bioactive glasses and Zn-doped glasses. J Therm Anal Cal. 2014;115:2137–44.
33. Stoch L, Stoch Z, Wacławska I. Silicate glass fertilizer. Patent PL 185 229 B1. 2003 [Polish].
34. Kabata Pendias A, Pendias H. Biogeochemistry of trace elements. Warsaw: Polish Scientific Publishers (PWN); 1993 (in Polish).
35. Görlich E. The effective charges and the electronegativity. Krakow: Polish Academy of Art and Science; 1997.
36. Stoch L. Thermal analysis and thermochemistry of vitreous into crystalline state transition. J Therm Anal Cal. 2004;77:7–16.
37. Brow RK, Click CA, Alam TM. Modifier coordination and phosphate glass networks. J Non-Cryst Solids. 2000;274:9–16.
38. Barin I, Knacke O. Thermochemical properties of inorganic substances. Berlin: Springer; 1973.